Carbohydrate Polymers 90 (2012) 218–223

Contents lists available at SciVerse ScienceDirect

Carbohydrate Polymers

journal homepage: www.elsevier.com/locate/carbpol

A kinetic model for oxidative degradation of bagasse pulp fiber by sodium periodate

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ARTICLE INFO

Article history:
Received 10 January 2012
Received in revised form 12 April 2012
Accepted 5 May 2012
Available online 11 May 2012

Keywords:
Dialdehyde cellulose
Periodate
Cellulose fiber
Degradation
Kinetics
Dynamic model

ABSTRACT

In this paper, some key parameters, such as the system pH, the periodate concentration, and the reaction temperature, on the influence of the bagasse fiber degradation were studied based on the oxygenant of periodate. And the feasible reaction mechanism was also discussed through the FTIR characterization for bagasse fiber before and after the oxidizing reaction. As the results shown, the crystallinity of bagasse fiber decreased with the oxidation level increasing. It was interesting that the aldehyde content of the reaction system rose gradually along with cellulose degradation. Based on this result, the selective oxidation kinetics was constructed by introducing of variable factor *R* (the ratio of aldehyde content to the degradation of cellulose fiber), and the results shown that there was a better correlation between the dynamic model and the experimental data, so the oxidation degree of bagasse fiber oxidized by periodate can be quantitative evaluated based on this model.

1. Introduction

Cellulose oxidized by sodium periodate has been extensively studied, as the C-2 and C-3 vicinal hydroxyl groups on the chain of cellulose could be selectively cleaved (Chavan, Sarwade, & Varma, 2002; Kim, Wada, & Kuga, 2004; Potthast, Kostic, Schiehser, Kosma, & Rosenau, 2007; Vicini et al., 2004). The product obtained by cellulose oxidation commonly refers to "dialdehyde cellulose". With rich reactivity of aldehyde group, dialdehyde cellulose could be further modified (Kim and Kuga, 2001; Wu and Kuga, 2006).

In the studies on the influence factors for preparing dialdehyde cellulose, it shows the optimum pH was the initial pH of 4.45 and the final pH of 3.20 (Maekawa and Koshijima, 1984), and the important factors to control the oxidation level were the periodate concentration and temperature Varma and Kulkarni (2002). But yet the high temperature and acid can make the cellulose or dialdehyde cellulose degraded. In the process of preparation, the crystallinity of the oxidized cellulose decreased with the oxidation level increasing (Kim, Kuga, Wada, Okano, & Kondo, 2000), and the yield declined as well (Li, Wu, Mu, & Lin, 2011). In addition, the dialdehyde cellulose is unstable and its molecular weight decreased significantly in hot water for a long time (Kim et al., 2004). However, to the best of our knowledge, there is little information available concerning on the kinetics of periodate oxidizing cellulose fibers from the view of aldehyde generation and cellulose degradation.

Therefore, in this work, the factors for sodium periodate oxidizing bagasse fiber were investigated by introducing of variable factor *R* (the ratio of aldehyde content to the degradation of cellulose fiber). Additionally, the kinetic models, based on the view of aldehyde generation and cellulose degradation, were built and compared with the experimental data.

2. Experimental

2.1. Materials

Cellulose fiber of bleaching bagasse pulp (obtained from Nanning Sugar Industry Co., Ltd. China.) of 60–80 mesh was used in this study. All chemicals, including sodium periodate (from Tianjin Yongda Chemical Reagent Co., Ltd., China), potassium permanganate and sodium carbonate (from Tianjin Kernel Chemical Reagent Co., Ltd., China), were obtained from commercial sources. All the reagents were of analytical grade without being further purified. Distilled water was used in solution preparation.

2.2. Methods

2.2.1. Preparation of 2,3-dialdehyde cellulose fiber

The 2,3-dialdehyde cellulose fiber was prepared by sodium periodate (Varavinit, Chaokasem, & Shobsngob, 2001). 5 g cellulose

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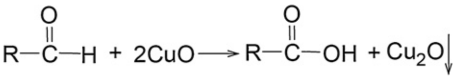
http://dx.doi.org/10.1016/j.carbpol.2012.05.027

fiber was added into 300 mL the sodium periodate solution and stirred with a magnetic stirrer in a water bath at the desired temperature. After the reaction, the product was washed several times with distilled water and dried at room temperature.

2.2.2. Determination of aldehyde content

The aldehyde content was determined according to the method for copper number (Cu#) following the Tappi standard method T 430; the reaction was as Eq. (1) (Chai, Zhang, Hou, & Yoon, 2007; Methods, 1989). The aldehyde content was calculated by Eq. (2).



$$\mathrm{R{-}\overset{O}{\overset{\|}{C}}{-}H} + 2\mathrm{CuO} \longrightarrow \mathrm{R{-}\overset{O}{\overset{\|}{C}}{-}OH} + \mathrm{Cu_2O}\downarrow \quad (1)$$

$$F(\%) = 0.2027 \times \mathrm{Cu\#} = \frac{0.3135 \times (V - B) \times C}{W} \times 100 \quad (2)$$

where F (%) is the percentage of aldehyde content; V (mL) and B (mL) is the volumes of potassium permanganate ($KMnO_4$) solution to titrate the filtrate of sample and blank; C (mol/L) is the concentration of $KMnO_4$; W (g) is the weight of testing cellulose sample.

2.2.3. Determination of loss rate of cellulose fibers

The loss rate of fibers (L) was calculated by the weight ratio of cellulose fibers after (w_a) and before (w_b) reaction, as Eq. (3).

$$L(\%) = \frac{w_b - w_a}{w_b} \times 100 \quad (3)$$

2.2.4. FTIR spectroscopy and crystallinity index

2 mg of cellulose samples were prepared by mixing with 200 mg of spectroscopic grade KBr. FTIR spectra were recorded using a Perkin Elmer BXII spectrum with the detector at 4 cm^{-1} resolution and 8 scans per sample from 400 to 4000 cm^{-1}.

Crystallinity index (CI) obtained by FTIR, was evaluated from the ratios of the absorption bands at 1429 cm^{-1} and 893 cm^{-1} (A_{1429}/A_{893}) (Hou, Liu, Liu, & Bai, 2007; Oh et al., 2005). Absorbance of the band obtained was automatically calculated at the maximum absorbance found by sensitivity of 100 using OMNIC 8.2 software.

3. Results and discussion

3.1. Effect of pH value

Glycoside bonds between units of cellulose are easily activated and cleaved under acidic conditions, especially for the cellulose with the carbonyl group on the main chain, which results in the degradation of cellulose. It can be seen clearly that there was enough H^+ for sodium periodate to oxidize the cellulose fibers in order to obtain the aldehyde content of about 16.18% when the pH was 2 (Fig. 1). However, the acid resulted in hydrolysis of cellulose, and made fiber loss 25%. While the acidity decreased, the hydrolysis could be inhibited. Hence, as pH came up to 4, the aldehyde content increased from 16.18% to 20.5%, but the loss rate of cellulose decreased from 25% to 8.71%. In addition, at high value of pH (>4), while the acid hydrolysis of cellulose decreased, the oxidation of cellulose fibers by periodate was inhibited, which resulted in the low aldehyde content (<15%). Thus, the optimum acidity for preparing 2,3-dialdehyde cellulose fiber by periodate was at pH 3–4.

3.2. Effect of the concentration of periodate

Natural cellulose is oxidized by sodium periodate to cleave C2–C3 bond of the glucose residue and produces aldehyde groups with the loss of cellulose. To avoid the effect of aldehyde group from thermal degradation of cellulose fibers, the experiments were carried out at room temperature. The contour plots of the aldehyde content and the loss rate of the cellulose show the same trend (see in Fig. 2(a)). The rate of oxidation reaction was dramatically enhanced with increasing concentration of periodate. Thus, the aldehyde content was raised from 2% to 12% while the concentration of periodate increased from 0.2 mol/L to 0.8 mol/L in 2 h. However, a little change of aldehyde content can be observed at each concentration level of periodate while reaction time was prolonged. That would be explained according to the studies from Calvini (Calvini, Conio, Princi, Vicini, & Pedemonte, 2006). It was found that there were three reactions occurred in the periodate oxidation system. The fast initial attack of periodate was in the amorphous region of cellulose, the second was a slow reaction attributed to the oxidation of the surface of crystallites, and the third was a slow reaction due to the oxidation of the crystalline core. The crystallinity of cellulose was easily disrupted by acid but blocked the effects of the periodate oxidation. The oxidation of the amorphous region of cellulose was improved by the periodate in high concentration levels. Thus, high concentration of periodate could increase the aldehyde content. When reaction proceeded to 6 h, the aldehyde content was 6% with 7% fiber loss at 0.2 mol/L periodate and 14% with 12% fiber loss at 0.8 mol/L periodate (Fig. 2(a) and (b)). Therefore, the medium aldehyde content with less degradation of cellulose can be obtained at low concentration of periodate for a long reaction time or at the high concentration of periodate for a short reaction time.

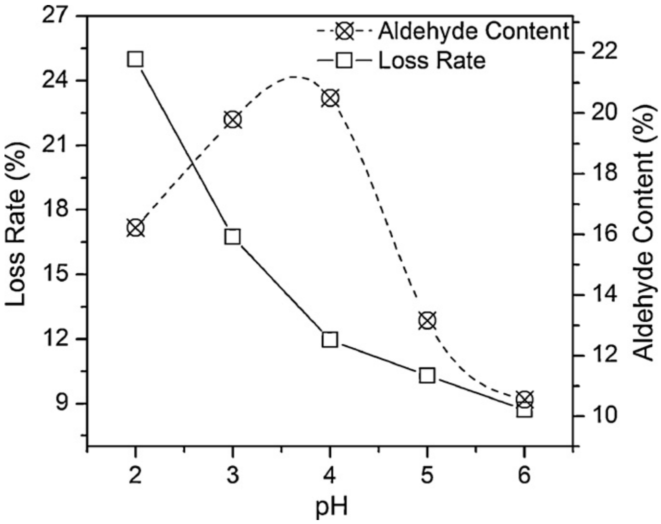


Fig. 1. The aldehyde content and the loss rate of cellulose at different pH (40 °C; periodate concentration, 0.6 mol/L; reaction time, 6 h).

3.3. Effect of reaction temperature

The rising temperature can increase the reaction rate. It shown the same trend of aldehyde content and the loss rate of the cellulose in Fig. 3. At room temperature, the oxidation reaction proceeded very slowly. Sirvio, suggested that the higher aldehyde contents could be achieved at elevated temperatures (Sirvio, Hyvakko, Liimatainen, Niinimaki, & Hormi, 2011). Thus, while at high temperature (45 °C), 10% aldehyde content could be obtained for 4 h, which was a simple and rapid method comparing to 4% aldehyde content at 25 °C for 9 h (Fig. 3(a)). However, the hydrolysis was also activated, which resulted in the loss of fiber. Accordingly, there were about 2% aldehyde content with 5% fiber loss at 25 °C for 6 h and 12% aldehyde content with 35% fiber loss at 45 °C for 6 h (Fig. 3(b)). Therefore, it can be concluded that temperature can

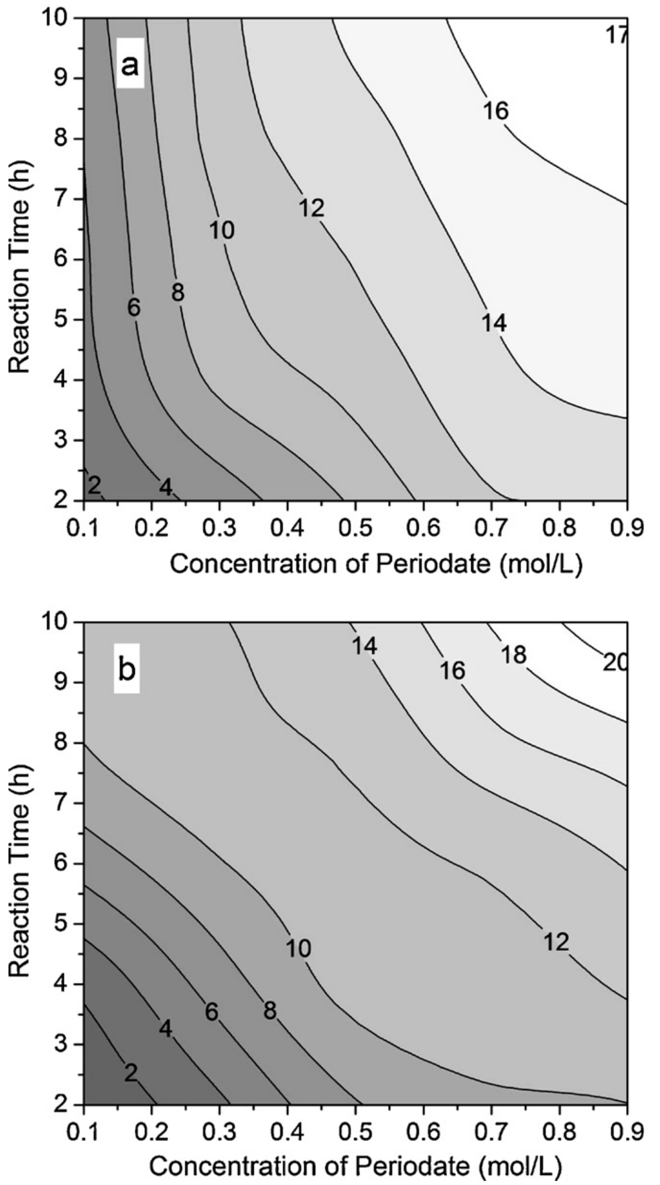


Fig. 2. The contour plots of the aldehyde content (a) and the loss rate of fiber (b) at different periodate concentrations (initial pH 3, room temperature).

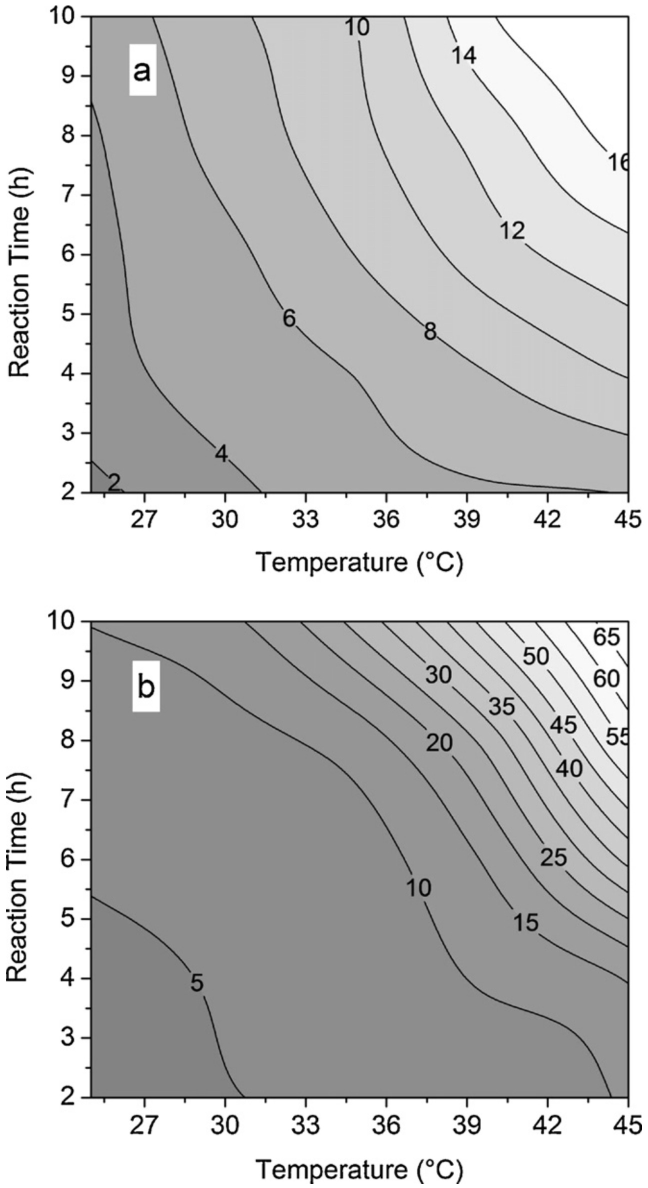


Fig. 3. The contour plots of the aldehyde content (a) and the loss rate of fiber (b) at different temperature (initial pH 3; periodate concentration, 0.6 mol/L).

improve the oxidation of cellulose fiber to achieve relatively high aldehyde content, but the fiber is degraded seriously.

3.4. *FTIR spectroscopy and crystallinity index*

FTIR was performed to characterize the changes of function groups and crystallization index (*CI*) of cellulose. As shown in Fig. 4, the main bonds in all samples can be assigned to (Schwanninger, Rodrigues, Pereira, & Hinterstoisser, 2004): 3450–3500 cm^{-1} (—OH stretching, H-bond), 2900–2945 cm^{-1} (C—H stretching of —CH_2 and C—H groups), 1734 cm^{-1} (C=O stretching vibration), 1654 cm^{-1} (water —OH bending vibration), 1429 cm^{-1} (—CH_2 symmetric bending vibration), 1373 cm^{-1} (C—H bending vibration), 1167 cm^{-1} (anti symmetric bridge C—O—C stretching vibration), 1024 cm^{-1} (C—O—C stretching vibration, ring deformation vibration) and 890–860 cm^{-1} (C—H deformation vibration of unite rings and (C=O)—H).

After 2 h reaction, the noticeable peak at 1734 cm^{-1} arises, which indicated the formation of C=O. The change of C—H vibration at 1373 cm^{-1} band with red shift at 893 cm^{-1} implied the cellulose

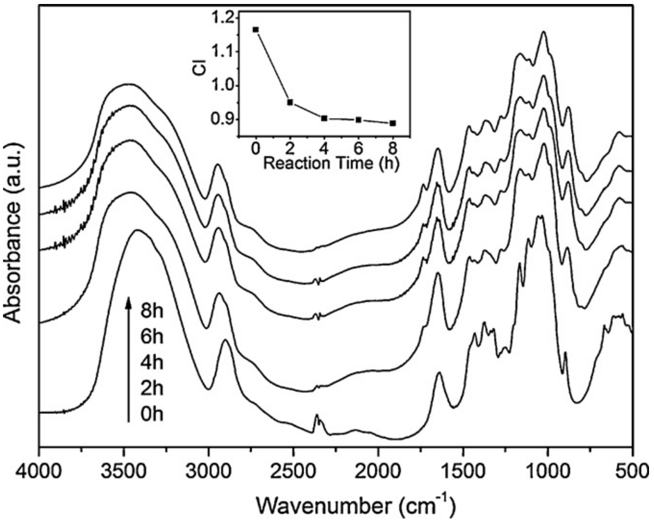


Fig. 4. FTIR spectra of cellulose fiber oxidation by periodate.

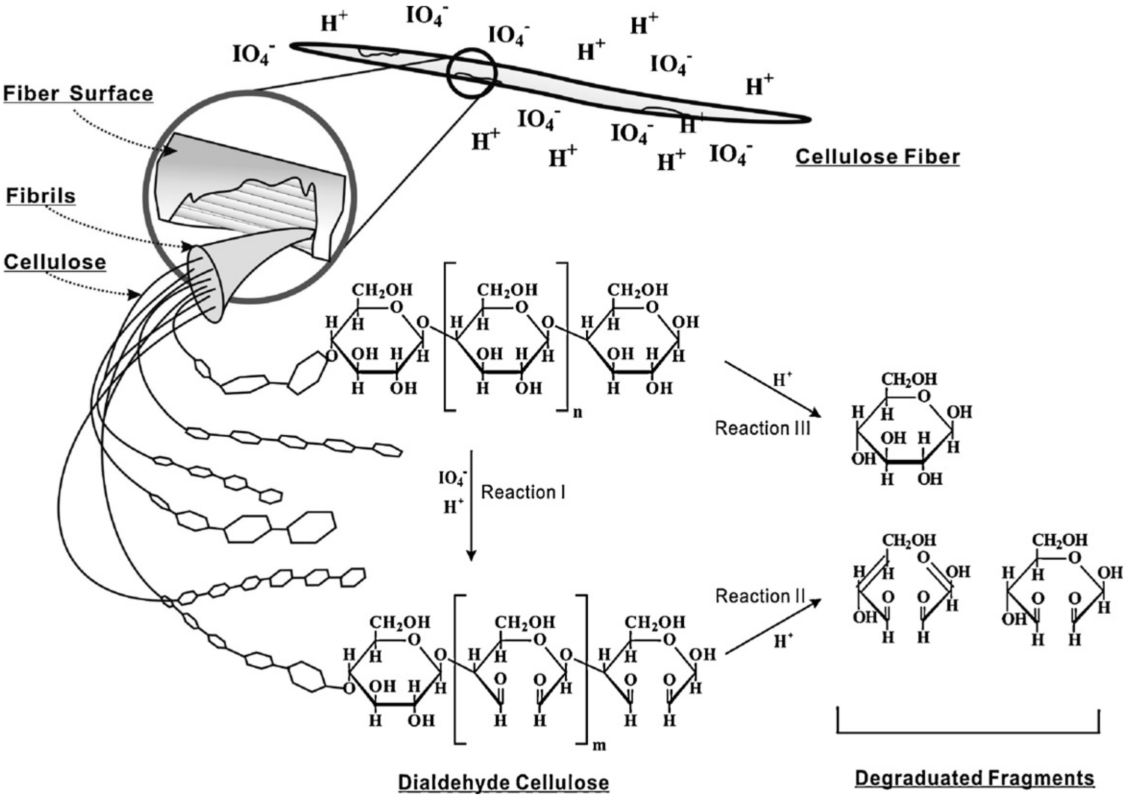


Fig. 5. The reactions of cellulose fiber oxidized by periodate.

skeletal changed on the main chain. In addition, the most pronounced changes in intensities are observed for bands at 1167 cm^{-1} with smaller changes at the 1024 cm^{-1} frequencies, which mainly due to C—O—C stretching vibration. It suggested the accelerated degradation of cellulose.

Crystallinity index (*CI*), determined by FTIR, decreases from 1.16 down to 0.88 (see in Fig. 4), which is considered to be the results of periodate oxidation and hydrolysis. Kim proved that the crystallinity of the crystalline cellulose decreased according to the oxidation level (Kim et al., 2000). The crystallinity of cellulose was disrupted by breaking hydrogen bonds in alpha-cellulose, opening up the structure and making more beta-(1,4)-glycosidic bonds readily accessible to the dilute acid (Zhao et al., 2006).

3.5. Kinetics of periodate oxidize cellulose fiber

Under acidic condition, the dialdehyde cellulose is obtained by oxidative cleavage of the bonds at the C-2 and C-3 of the anhydro D-glucopyranose residues, as Reaction I (Fig. 5). Additionally, glycoside bonds between units of cellulose are easily cleaved by beta-cleavage reaction (Reaction II) and acid hydrolysis (Reaction III) which lead the loss of cellulose (Maguire, 1977; Sasaki et al., 1998; Singh, Ray, & Vasudevan, 1982). The reactions can be referred to degradation reaction. Thus, in order to achieve the 2,3-dialdehyde cellulose by periodate, the reaction of selective oxidation is going on with the degradation of cellulose and the change of polymerization degree.

The reactions of cellulose fibers could be assumed to perform independently, and the reaction equations are in a general way as system (4).

$$\mathrm{Glc} + \mathrm{IO_4}^- \xrightarrow{H^+} \mathrm{DGlc} + \mathrm{IO_3}^- + \mathrm{H_2O} \quad \text{rate constant} = k_1 \tag{4.1}$$

$$\mathrm{Glc} \xrightarrow{H^+} \mathrm{LO} \quad \text{rate constant} = k_2 \tag{4.2}$$

$$\mathrm{DGlc} \xrightarrow{H^+} \mathrm{LDO} \quad \text{rate constant} = k_3 \tag{4.3}$$

where Glc is the cellulose chain on the fiber, DGlc is the 2,3-dialdehyde cellulose on fiber; LO and LDO are the oligose obtained by the degraded cellulose and dialdehyde cellulose, k_1, k_2 and k_3 are the rate constants. The equations of kinetics can be expressed as system equation (5).

$$\frac{d[\mathrm{DGlc}]}{dt} = k_1[\mathrm{Glc}][\mathrm{IO_4}^-] - k_3[\mathrm{DGlc}] \tag{5.1}$$

$$\frac{d[L]}{dt} = \frac{d[\mathrm{LO}]}{dt} + \frac{d[\mathrm{LDO}]}{dt} = k_2[\mathrm{Glc}] + k_3[\mathrm{DGlc}] \tag{5.2}$$

$$-\frac{d[\mathrm{IO_4}^-]}{dt} = k_1[\mathrm{Glc}][\mathrm{IO_4}^-] \tag{5.3}$$

The reactions occurred on the surface of fiber classed as solid–liquid heterogeneous reaction. The activity of cellulose or dialdehyde cellulose is depended on the activity parts on the surface of cellulose and the acidity. Thus, it is assumed that: the oxidation reaction is pseudo first order, and the degradation reaction is pseudo zero order. It is convenient to use the activity coefficient (α) for each of the two processes in the calculations (see in Eqs. (6.1) and (6.2). We further assume, as a first approximation, that the rate constants and the activity coefficients are independent of the chemical composition of the cellulose.

$$[\mathrm{DGlc}] = C_0(1 - \exp(-\alpha_1 K_1 t)) - \alpha_3 K_3 t$$
$$(K_1 = k_1[\mathrm{fiber}], K_3 = k_3[\mathrm{fiber}]) \tag{6.1}$$

$$[L] = (\alpha_2 K_2 + \alpha_3 K_3)t \quad (K_2 = k_2[\mathrm{fiber}]) \tag{6.2}$$

As generation of aldehyde was associated with the degradation of cellulose, the ratio (*R*) of the

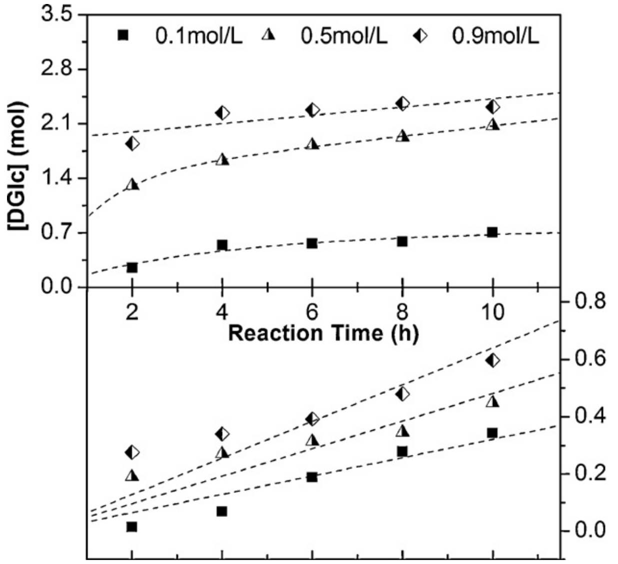


Fig. 6. Experimental (symbols) and fitted (dotted lines) data for periodate oxidized the cellulose fiber for [DGlc] and [L] at different periodate concentrations (initial pH 3, room temperature).

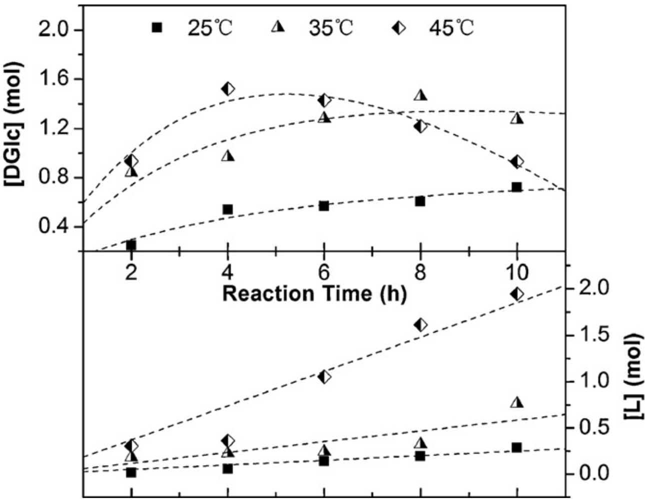


Fig. 7. Experimental (symbols) and fitted (dotted lines) data for periodate oxidized the cellulose fiber for [DGlc] and [L] at different temperature (initial pH 3; periodate concentration, 0.6 mol/L).

aldehyde generated to the dose of cellulose degraded, as shown in Eq. (6.3), is introduced to illustrate the efficiency for preparing 2,3-dialdehyde cellulose.

$$R = \frac{[\mathrm{DGlc}]}{[L]} = \frac{C_0(1-\exp(-\alpha_1 K_1 t)) - \alpha_3 K_3 t}{(\alpha_2 K_2 + \alpha_3 K_3)t} \tag{6.3}$$

Furthermore, assumptions are made as follows: the fragments of degraded fiber are glucose units; the aldehyde groups are all generated by periodate oxidizing cellulose fiber; and the molecular weight of aldehyde and fraction of fiber loss are marked as M_a and M_b, respectively. [DGlc], [L] and R could be calculated by the percent of aldehyde content and cellulose loss, as Eqs. (7.1)–(7.3) shown.

$$[\mathrm{DGlc}] = \frac{m_{\mathrm{DGlc}}}{M_\mathrm{a}} = \frac{m_0 F(1-L)}{M_\mathrm{a}} \tag{7.1}$$

$$[L] = \frac{m_L}{M_\mathrm{b}} = \frac{m_0 L}{M_\mathrm{b}} \tag{7.2}$$

$$R = \frac{[\mathrm{DGlc}]}{[L]} = \frac{M_\mathrm{b} m_{\mathrm{DGlc}}}{M_\mathrm{a} m_L} = \frac{M_\mathrm{b}}{M_\mathrm{a}} \cdot \frac{F}{L} \cdot (1-L) \tag{7.3}$$

The system equation (6) was used to fit the experimental data calculated by system equation (7) to explain the kinetics of the reactions, using ORIGINPRO 8.5 software.

The trends for aldehyde generated climb up slow at concentration of periodate 0.1 mol/L (see in Fig. 6), but it seems to be linear while the concentration is 0.9 mol/L. The data fitted the kinetic curve of aldehyde generation well and the values of the regression coefficients were higher than 0.90 except for 0.9 mol/L for 0.31. However, the experimental data do not fit the kinetics of cellulose degradation (see in Fig. 6), while the relationship between fiber loss and time seems to be linear with almost the same slop. It would be considered to result from the structure change of cellulose fiber destroyed by the periodate at the high concentration (0.9 mol/L). Furthermore, the amorphous region of cellulose was easily activated by the theory of Calvini et al. (2006). It reacted at the preliminary stage resulted in the degradation. The crystalline region inhibited the reaction of oxidation and degradation. However, the oxidation of cellulose was a self-accelerating process (Kim et al., 2000) and the decreases of crystallinity improved the accessibility and reactivity of cellulose fiber. Thus, while the concentration of periodate is 0.9 mol/L, the aldehyde content climbed up to 2 mol in 2 h and influences the process of cellulose degradation at initial stage.

The data were overlapping for aldehyde generation and cellulose degradation at the reaction temperature blow 35 °C. With the increased temperature at a higher level (>35 °C), the aldehyde generated rapidly and then slowed down. There is a peak at 4 h for 45 °C (see in Fig. 7). However, the experimental data fitted the kinetic curves well with the values of the regression coefficients above 0.90 for aldehyde generation, 0.8 for degradation. It could be explained by the Arrhenius equation ($K = A\exp(-E_\mathrm{a}/RT)$), which gives the relation between K and T. The rate constant (K) increased as the elevated temperature actives the reactions of aldehyde generation and cellulose degradation. Then the cellulose degradation changed the surface structure of cellulose fiber with the changing of the activity coefficient at the same time. Thus, the experimental data deviated from the fitted kinetic curve of cellulose degradation at 35 °C and above.

Based on the study, the relationship between aldehyde generation and cellulose degradation is very close in periodate oxidizing cellulose fiber. R was used to evaluate the condition for preparing dialdehyde cellulose fiber. The concentration of periodate makes a little effect for R, and the fitted curve by equations is almost overlapping the experimental data in Fig. 8(a). R values have the trend toward 4, with the reaction time from 2 h to 10 h at concentration of periodate from 0.1 to 0.9 mol/L, indicating that the cellulose degradation rate was increased.

While the ratio R >1, the rate of the aldehyde generation reaction is higher than that of cellulose degradation reaction, which means the more aldehyde obtained with less fiber loss. Therefore, while changing the concentration of periodate from 0.3 mol/L to 0.9 mol/L, the reaction of aldehyde generation was faster than cellulose degradation in 10 h.

It shows the elevated temperatures makes the experimental data deviate from the kinetic curve of cellulose degradation, which considered to be the effect of thermal degradation of cellulose in Fig. 8(b). Additionally, the ratio R tends to below 1 at 35 °C for 10 h and at 45 °C for 6 h, which indicated that the cellulose degradation reaction was dominant. Thus, high temperature can improve the aldehyde content of dialdehyde cellulose fiber, while the ratio R below 1 in short reaction time suggested that high temperature was helpful to the degradation of cellulose.

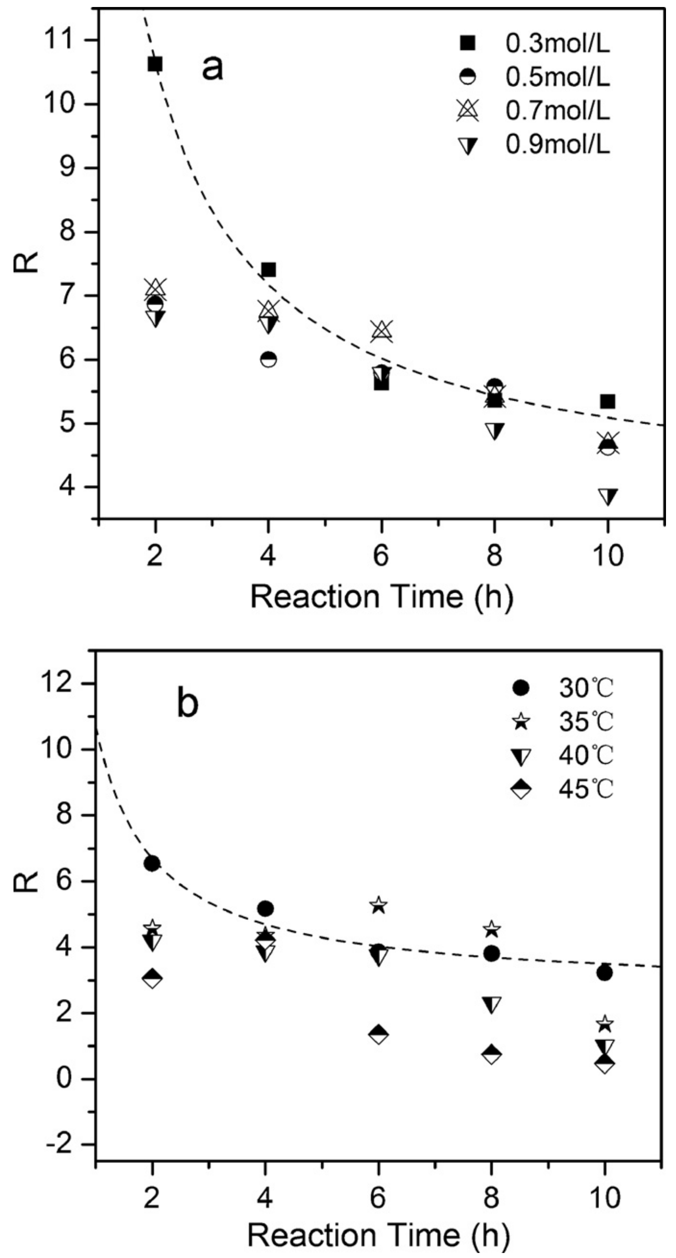


Fig. 8. Experimental (symbols) and fitted (dotted lines) data for *R*: (a) at different periodate concentrations and (b) at different temperatures.

4. Conclusions

Increased concentration of periodate and elevated temperature can shorten the reaction time to achieve a relatively high yield of 2,3-dialdehyde cellulose fiber. However, comparing the dynamic model with the experimental data, the *R* value tends to 4 at the concentration range of periodate between 0.3 and 0.9 mol/L, which indicated that the reaction rate of aldehyde generation was higher than that of degradation. Furthermore, the ratio *R* is below 1 at 45 °C for 6 h, as the aldehyde content could be improved by rising temperature, but the degradation of cellulose was accelerated. In addition, The cellulose crystallization index, determined by FTIR, decreased from 1.16 down to 0.88 with the increase of the oxidation level. Thus, in further studies, whether experimental or industrialized research, much attention should be paid to fiber loss by periodate oxidizing cellulose fiber.

Acknowledgements

This work was financially supported by the National High Technology Research and Development Program (863 Program) (2009AA06A416) & (2010GXNSFE 013006), National Water Special Research Program (2008ZX07317-02-03A2), Innovation Project of Guangxi Graduate Education (GXU11T31079) and Research Funds of the Guangxi Key Laboratory of Environmental Engineering (0804K016). Gratitude is expressed to Prof. Hongxiang Zhu of Guangxi University, China, who reviewed and checked this paper carefully.

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